REMARKS

In the Official Action, the Examiner withdrew certain of the previous rejections, maintained others, raised a new rejection under the first paragraph 35 U.S.C. § 112, and indicated the allowability of claim 11. While applicants certainly appreciate the favorable indication with respect to claim 11, applicants respectfully submit that all of the claims of record are patentable in view of the following discussion and the documents that are concurrently being submitted herewith.

Addressing each of the rejections in the order in which they appear in the Official Action, applicants note that the rejection under the first paragraph of 35 U.S.C. § 112 is based on the Examiner's hypothetical situation that one can perform a sealing treatment on the pores of the anodic film and lessen the pore diameter wherein the pores have a mouth diameter of 35 nm and an inside diameter of 20 nm.

Based on a proper understanding of the pore structure and the effect of a sealing treatment, it is apparent that the claims of record define a structure that is clearly supported by the present specification. More precisely, as set forth in the first full paragraph on page 2 of the specification, as originally formed, the pores of the formed anodic oxide film are generally pipe-like in structure in which the diameters at the surface part and at the maximum diameter part are almost the same. This understanding is confirmed by the technical literature article entitled

"Fabrication of Ordered Nanostructure Based on Anodic Porous Alumina."1 Figs. 1 and 5 of thid document illustrate an idealized model of the porous structure of anodic alumina and an actual cross-sectional view with such figures being reproduced hereafter:

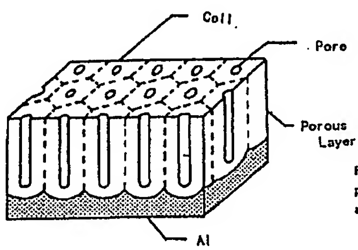


Fig. 1 Idealized model of porous Structure of anodic alumina

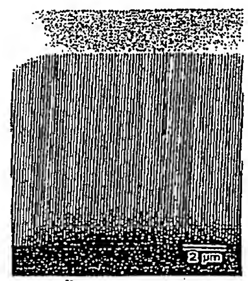
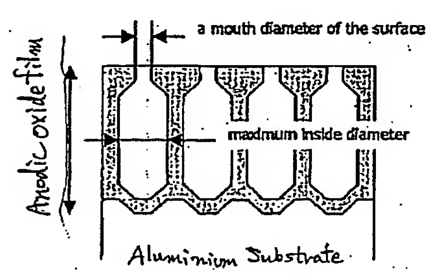


Fig. 5 Cross sectional view of cahannel-array of anodic alumina; 0.3 M oxalic acid, 17 ℃, 60 V

When a sealing treatment is performed on the surface mouth areas of the pores, as described on page 14, the average pore diameter of the surface mouth areas is decreased and it logically follows that the maximum inside diameter is larger than the surface mouth diameter with an illustrative structure being as follows:



1 Hideki MASUDA et al., SPIE Vol. 3511, pp 74-81, SPIE Conference on Micromachining and Microfabrication Process Technology IV, September 1998, Santa Clara, CA.

Accordingly, keeping in mind the caveat that the claimed subject matter need not be described in *haec verba* to satisfy the description requirement (see *In re Herschler*, 200 USPQ 711 (CCPA 1979) it is evident that the claims of record have proper descriptive support in the specification and applicants therefore respectfully request that the Examiner reconsider and withdraw the rejection under 35 U.S.C. § 112.

The Official Action next sets forth two rejections based on "obviousness-type" double patenting rejections over certain claims of two pending applications. While applicants do not necessarily agree with the Examiner's positions concerning these rejections, particularly in view of the claimed anodic oxide film with the defined pore configuration, applicants are hereby providing a Terminal Disclaimer relating to the two cited applications and such Terminal Disclaimer fully meets these rejections.

Turning to the next series of rejections, applicants call the Examiner's attention to the fact that the present application claims the benefit of various Japanese priority applications including Japanese Patent Application No. 2001-009871 filed on January 18, 2001 and Japanese Patent Application No. 2001-104632 filed on April 3, 2001. As may be seen from the verified English translations of these two applications, the presently claimed subject matter is entitled to at least these filing dates. For instance, the Examiner can compare the subject matter of claim 1 with the specification and particularly claim 1 of Japanese Patent Application No. 2001-104632. Claims 3-5 can be compared to the specification and claims 2-4 of the same '632 application. The void ratio defined in claims 6 and 9 and the defined anodic oxidation treatment of claim 7 is supported by the specification and claims 5 and 6 of the '632 application. The '871 application also describes the

claimed void ratio of claims 6 and 9 (see claim 2) with the particle layer and other aspects of the remaining claims also being evident in the specification and claims of the '871 application. Since the filing dates of these Japanese priority documents precede the U.S. filing dates of U.S. Patent Application Publication No. 2002/0033108 and U.S. Patent Application Publication No. 2002/0039702, it is evident that neither of these documents can be relied on to support a "prior art" rejection of any of the claims.2

With regard to the last remaining rejection based on U.S. Patent Application Publication No. 2001/0041305, the Examiner has conceded that the '305 publication does not teach a number of the claimed features. In this respect, applicants refer the Examiner's attention to section [0083] which described micropores having a pore diameter of 5 to 10 nm (with claims relating to 1 to 5 nm pore diameter) which is substantially different from the maximum inside diameter of from 20 to 300 nm recited in claim 1. Accordingly, the "anticipation" rejection set forth in the Official Action cannot be maintained and, pursuant to the provisions of 35 U.S.C. § 103(c), a rejection under 35 U.S.C. § 103(a) also cannot be maintained (note the common ownership statement in the prior Amendment).

Since all issues raised in the Official Action are believed to be met by the instant submission of a Terminal Disclaimer, technical literature and verified translations of priority documents, applicants respectfully maintain that the instant

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2 It is to be understood that applicants do not necessarily concede the propriety of the Examiner's rejections and note that any potential rejection that could be based on 35 U.S.C. § 103(a) can be met via the provisions of 35 U.S.C. § 103(c).

response is proper in all regards and therefore request entry and allowance of the present application.

Should the Examiner wish to discuss any aspect of the present application, he is invited to contact the undersigned attorney at the number provided below.

Respectfully submitted,

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Invited Paper

Fabrication of Ordered Nanostructure Based on Anodic Porous Alumina

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ABSTRACT

A highly ordered nanochannel array structure with high aspect ratios was fabricated based on the anodization of aluminum. A texturing treatment of the Al surface was carried out by nanoindentation process using the SiC mold initiated the development of an ideally-arranged-hole-array structure of anodic porous alumina. The hole-array has ideal hexagonal arrangement over millimeter dimensions, and the aspect ratio of the channel was over 150. In this report, the fabrication of the highly ordered nanochannel array and the application of the obtained structure to the preparation of nanostructures are described.

Keywords: Anodic Porous Alumina, Ordered Structure, Nanochannel Array, Replication

1. INTRODUCTION

There has been growing interest in the fabrication of highly ordered structures with dimensions ranging from the submicrometer to nanometer scale. Such structures have a wide variety of applications in electronic, optoelectronic, and micromechanical devices. Further improvements in the fabrication process are required, however, especially for the fabrication of fine structure with a high aspect ratio. One way to simplify the fabrication of ordered fine structures in is to use a naturally occurring process in which self-organized ordered structures are used[1-4], and various techniques have been proposed for such a process on a nanometer scale. However, with most of them the regularity of the obtained structure has not been satisfactory. In addition, there have been very few processes that can be applied to the fabrication of ordered structure with a high aspect ratios.

Anodic porous alumina membranes formed by anodizing Al in an acidic electrolyte have unique properties[5]; they have an ordered porous structure composed of a closely packed array of columnar hexagonal cells, each containing a central cylindrical hole as shown in Fig.1. The size of the hole in the membrane is very fine (5-200 nm) and the size distribution is extremely narrow. The dimensions of the porous structure of the films depend on the formation conditions, i.e., the electrolyte composition, applied voltage, and temperature. The cell size, which is directly related to the density and spacing of the holes, is directly related to the anodizing voltage.

For applications of the hole-array structure of anodic porous alumina to device fabrication, a highly ordered array structure is essential so that the properties of the fabricated devices can be optimized. However, the geometry of the anodic porous alumina normally obtained is far from the idealized model in Fig.1; the arrangement of the cells and pores is not perfectly hexagonal. Recently one of authors reported that a highly ordered honeycomb structure with an almost ideal hexagonal arrangement can be naturally formed over relatively

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large areas under an appropriate anodizing condition[6,7]. This membrane with an ordered hole array structure has increased attractiveness as a starting material for nanofabrication.

The condition for the self-ordering of the cell configuration is characterized by a longer anodization period compared to the usual anodizing condition at an appropriate applied voltage. The self-ordering proceeds through the rearrangement of the cell configuration, which gradually changed from an almost random configuration at the initial stage of anodization to an ordered structure after steady-state oxide growth. Thus a longer period of anodizing improves the regularity of the hole arrangement and almost ideally arranges the hole-array structure. In the area of the defect-free configuration, there appears a domain structure, at the boundary of which the defects are accumulated. The domain grows with anodizing time, uptaking the neighboring cells.

The ordering of the hole arrangement is also dependent on the anodizing voltage, and the voltage required for the self-ordering is evidently dependent on the solution used for the anodization. The most appropriate voltage for the ordering of the hole arrangement in oxalic acid and sulfuric acid is 40 V and 25 V, respectively. Self-ordering of the hole arrangement could not be observed without the appropriate voltage conditions.

In this report, we present the results of the fabrication of the anodic porous alumina whose ordered hole-array structures are improved by a texturing process, and describe the preparation of fine nanostructures based on their ordered structures.

2. HIGHLY ORDERED HOLE-ARRAY USING TEXTURING PROCESSES

With naturally occurring self-ordering processes, the size of the defect-free area is limited to several micronmeters because the relatively large ordered area makes it difficult to rearrange the cell configuration after the long period of anodization. To improve the ordering of the hole configuration, we introduced a novel process which can precisely control the growth of the channel-array in the anodic porous alumina and enables us to produce a single-domain channel-array architecture on a millimeter scale[8].

The general concept of the fabrication of the single domain defect-free structure is outlined in Fig. 2. In this process, because the development of the hole is initiated at the initial stage of anodization by obtainning the appropriate texture of the surface (array of convexs) and the appropriate condition is kept for the self-ordering, the growth of the highly ordered hole-array architecture can be expected to form spontaneously. For the initiation points, we prepared an ordered array of concaves by a nanoindentation process using a mold that can be easily prepared with standard lithographic techniques. The shallow texture can introduce the development of holes and can guide the growth of the holes with an extremely high aspect ratio. The nanoindentation process using an appropriate master offers the possibility of high throughput mass production that can overcome the bottleneck in the conventional nanolitographic process.

The fabrication procedure for the ordered hole array structure is schematically shown in Fig. 3. The master in which the convexes are arranged in a hexagonal array, was fabricated with SiC using conventional EB lithography . The master is placed on an Al sheet and pressed with an oil press. This process generates an array of concaves on the surface of Al; the convexes in the master are replicated as concaves in the Al. The anodizing of Al was conducted under a constant voltage condition in an oxalic acid solution. After the anodization, the hole-array was observed after removing the Al substrate and the bottom part of alumina layer.

Figures 4 shows a typical example of a fabricated nanochannel array in the anodic

alumina. In this case, the anodizing was conducted under a constant voltage of 60 V after the texturing of a 150 nm period. From the SEM micrograph of the surface, it was confirmed that the capillaries are arranged in an ideal two-dimensional hexagonal configuration.

The cross-sectional view in Fig.5 demonstrates the higher aspect ratio feature of the channel-array. An important point in the present method is that shallow predetermined concaves (~20 nm) can initiate the development of the pore and can guide the growth of the long channel over 15 μm (aspect ratio of 150).

Figure 6 shows the channel array with a smaller interval (100 nm), which corresponds to the packing density of 10^{10} per square centimeter, obtained at anodizing voltage of 40 V. In this case, predetermined texturing corresponding to the anodizing voltage was adopted. If the anodizing condition deviates from the relationship between the cell size and forming voltage, which was described above, the growth of the ordered cell configuration can not be maintained. In addition, the self-ordering condition described above is also important for the formation of a channel-array with high aspect ratios in this process.

3. FORMATION OF PATTERNED HOLE-ARRAY STRUCTURE

When we apply the mold with the patterned texture to the indentation process, a hole-array structure with a patterned structure can be obtained. Figures 7 shows an example of a patterned hole-array structures in anodic porous alumina. After texturing using the SiC mold with the patterned array of convexes, the Al sheet was anodized. Figure 7 is a surface view of the hole-array structure of anodic alumina. This photograph confirms that the arrangement of the hole configuration can be controlled; the configuration in the textured area shows hexagonally arranged ordering, while the configuration in the nontextured area has no ordering of the hole-array.

These properties and the obtained structure will be applicable to the fabrication of optical guides that can control light propagation due to the periodicity of the structures.

4. FABRICATION OF ORDERED NANAOSTRUCTURE FROM ANODIC ALUMINA

The hole array structure of anodic porous alumina can be used as a starting material for the fabrication of nanostructures[9-15]. A two-step replication process using anodic porous alumina as a starting structure can generate a hole array structure of metals, semiconductors and polymers[6, 16-18]. In this process, the fabrication of negative-type anodic porous alumina and the subsequent formation of positive-type led to the formation of porous metal and semiconductor with a geometrical structure identical to that of the anodic porous alumina [Fig. 8]. An important aspect that distinguishes our process from the conventional one-step embedding method is that our process permits the full replication of the fine structure of the starting materials with desired materials.

Figure 9 shows an example of a fabricated ordered Au hole-array formed from the highly ordered anodic porous alumina. The obtained Au membrane has ideally arranged hole-array structure that corresponds to the anodic porous alumna used as the template. This process can be applied to the fabrication of various kind of metals (Au, Pt, Ni etc.,) and semiconductors (CdS, TiO_2 etc.,).

5. CONCLUSION

Anodization using a texturing process generates anodic porous alumina with an improved nanochannel-array architecture. The obtained anodic alumina has the almost ideal hole configuration. This technique will be suitable for the mass production of the restrictedly

ordered nanochannel arrays with high aspect ratios.

The ordered hole-array obtained by Al anodization or the replication process based on their ordered structure is one of the candidates for the two-dimensional photonic-band architecture. In addition, the highly ordered nanochannel-array will be a powerful tool in the development of nanodevices. Perfect periodicity is especially promising for the fabrication of huge data storage systems utilizing long range ordering, which is essential for the tracking of styluses.

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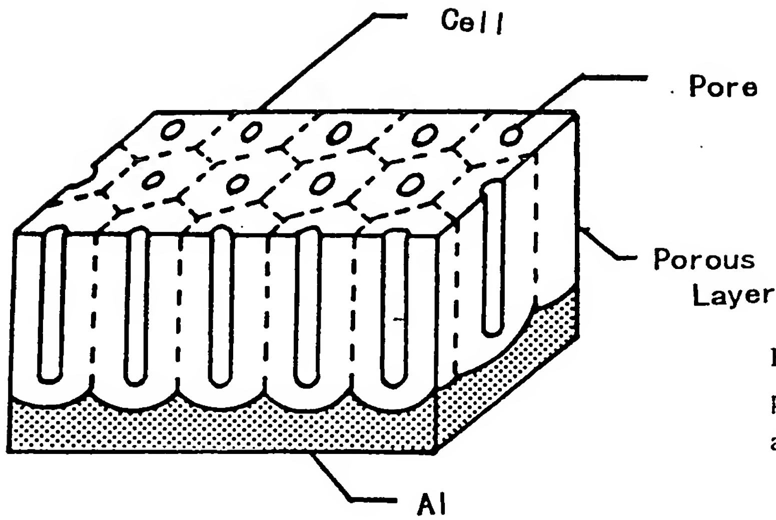

Fig. 1 Idealized model of porous Structure of anodic alumina

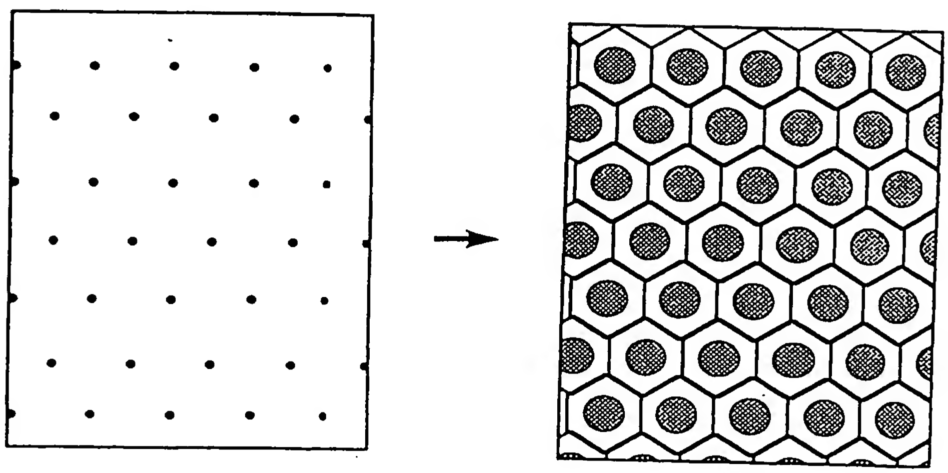

Fig.2 Schematic drawing of the fabrication of ideally ordered channel-array architecture in anodic alumina; textured surface of aluminum (a) and fabricated porous streucture (b).

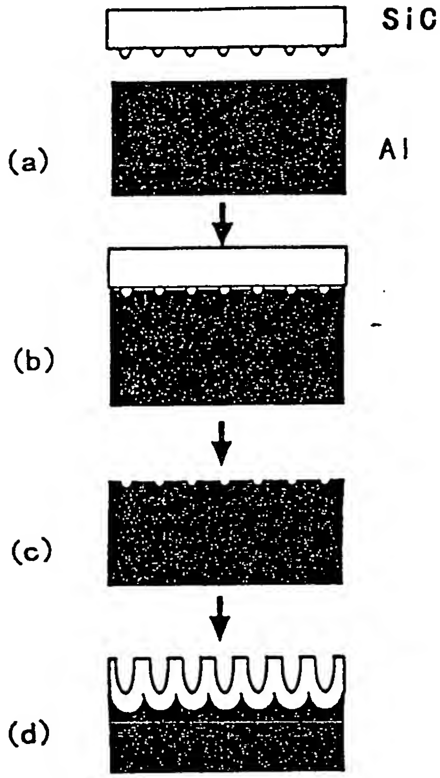

Fig.3 process for the fabrication of highly ordered nanochannel-array; SiC mold with hexagonally ordred array of convexes (a), molding on Al substrate, textured Al (c), anodization and growth of channel-array (d).

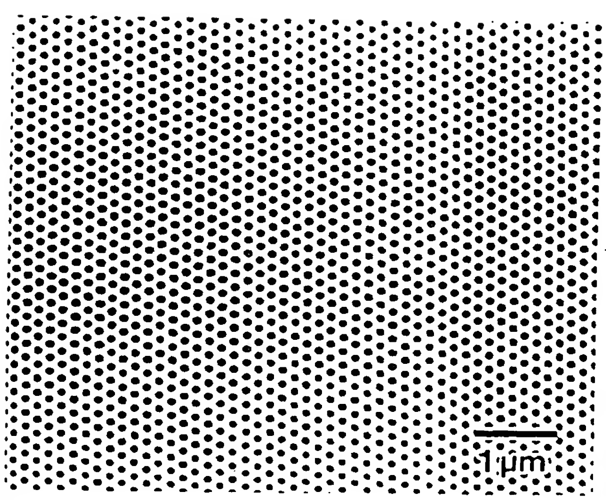

Fig. 4 SEM photograph of surface view of porous alumina; interval of texturing was 150 nm, 0.3 M oxalic acid, 17℃, 60V.

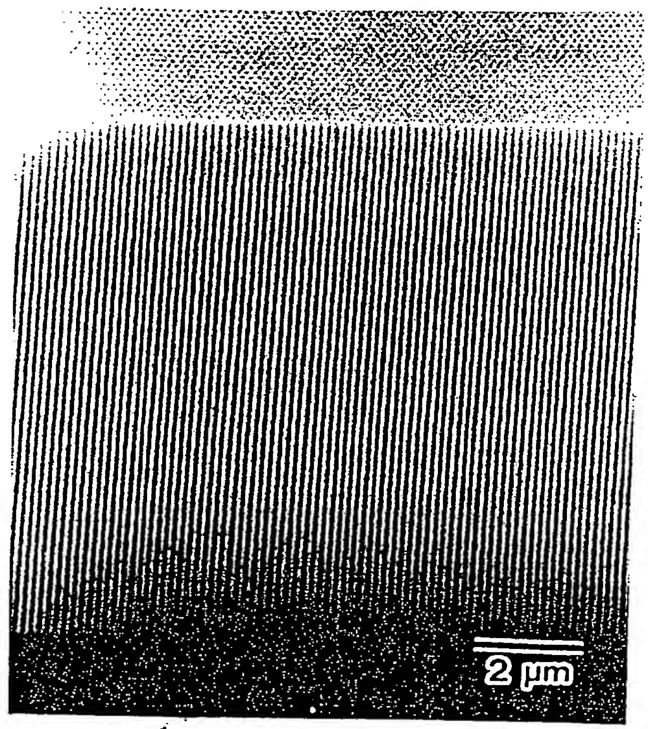

Fig. 5 Cross sectional view of cahnne-array of anodic alumina; 0.3 M oxalic acid, 17 ℃, 60 V

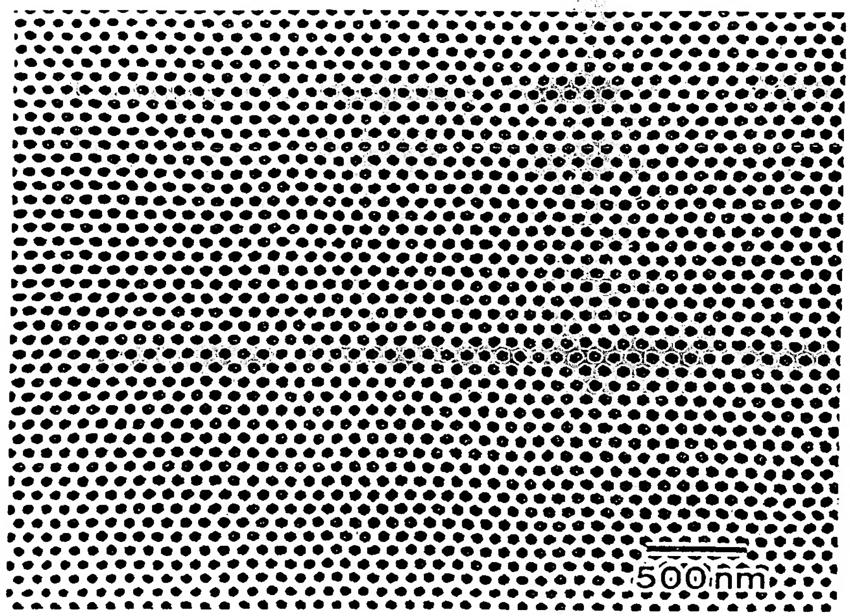

Fig. 6 SEM photograph of anodic porous alumina; interval of texturing was 100 nm, 0.3 M oxalic acid, 17 ℃, 40 V.

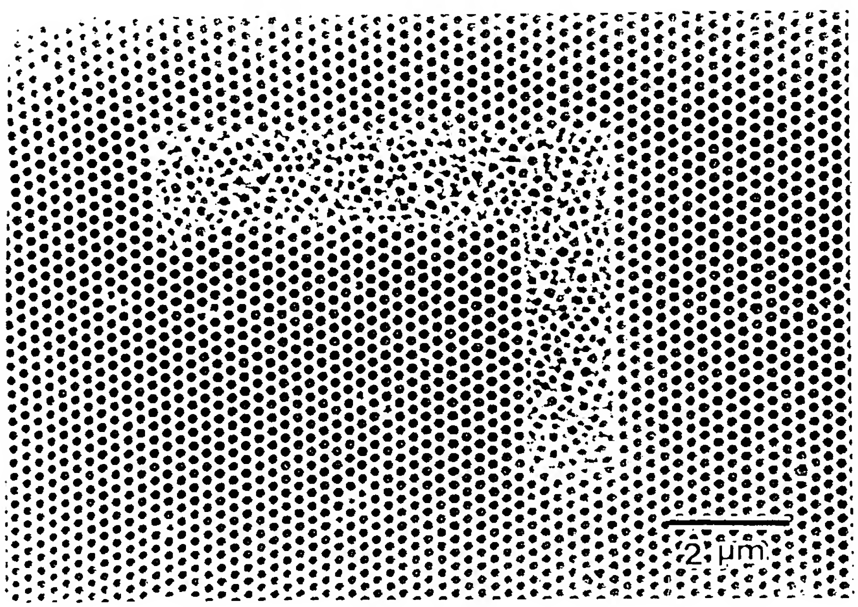

Fig. 7 SEM photographs of surface view of patterned hole-array.

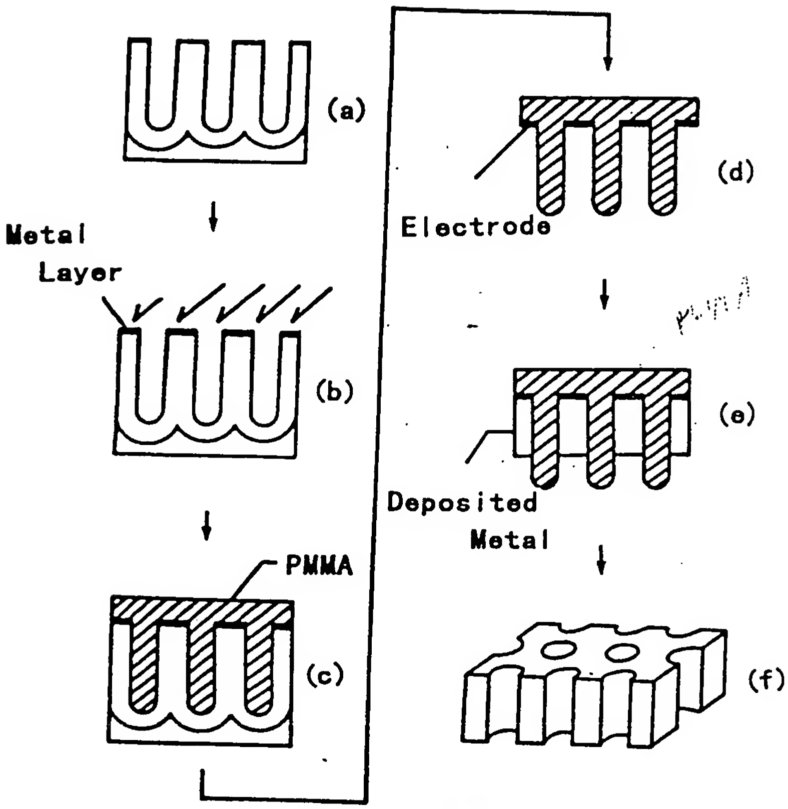

Fig. 8 Schematic diagram for two-step replication process for preparation of metal hole-array; porous alumina(a), Formation of metal layer(b), injection poymer[PMMA](c), negative type(e), metal deposition (e), Positive type (f) .

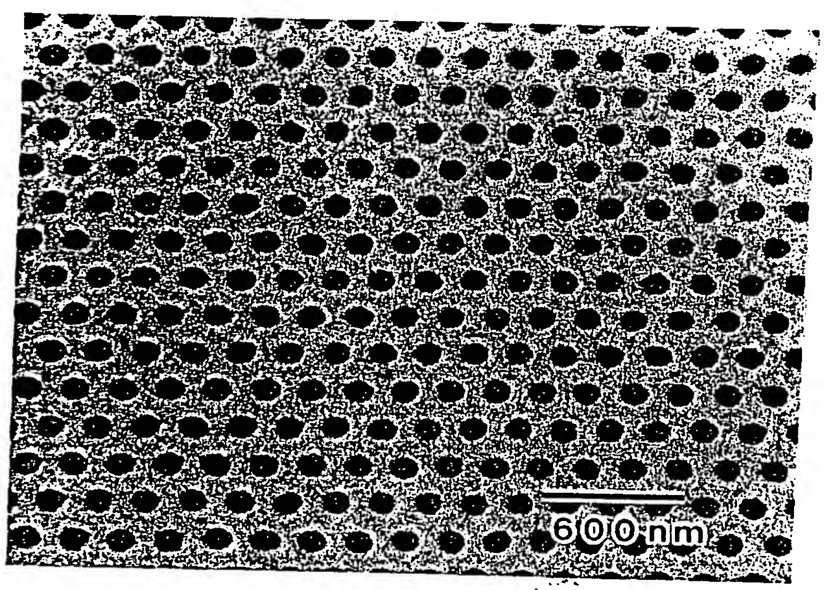

Fig. 9 SEM photograph of replicated Au hole-array from anodic porous alumina.